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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-025**
J. Boatz; K. Christe; R. Haiges; S. Schneider; T. Schroer; A. Vij; V. Vij; W.W. Wilson, "Towards New
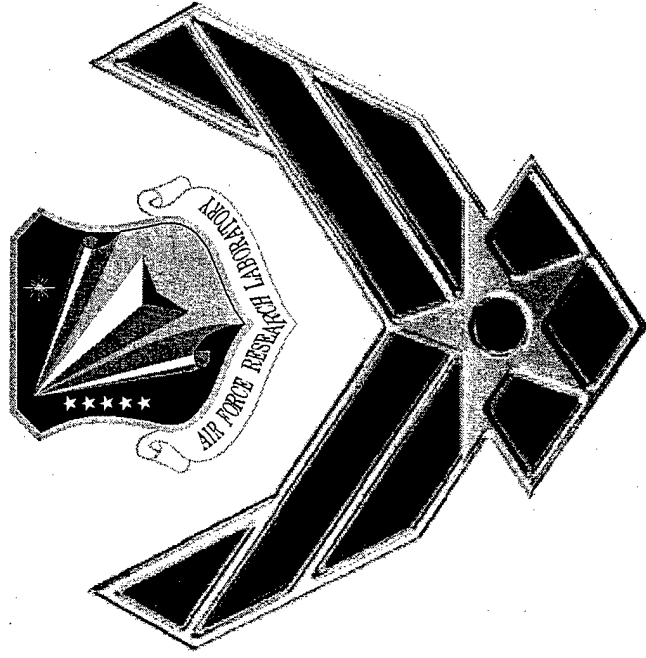Polynitrogen Species: The Search for Viable Precursors"

43rd Sanibel Symposium / ACS Meeting   (Statement A)
(St. Augustine, FL, 22 Feb thru 1 Mar 2003) (Deadline: 22 Feb 2003)

Towards New Polynitrogen Species:
The Search for Viable Precursors
43rd Sanibel Symposium, Feb 22 - March 1, 2003
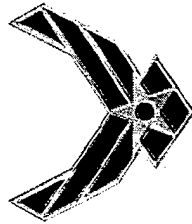
Dr. Jerry A. Boatz

Senior Research Chemist

Propellants Branch

Air Force Research Laboratory

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(661) 275-5364

New Polynitrogen Compounds

Karl Christe[a,b], Ralf Haiges[a,b], Stefan Schneider[a,b], Thorsten Schroer[a,b], Ashwani Vij[a], Vandana Vij[a], and William W. Wilson[a]

[a] Air Force Research Laboratory

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[b] Loker Hydrocarbon Research Institute

University of Southern California

Los Angeles, CA 90089
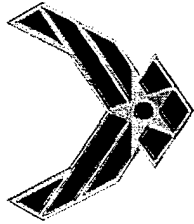
High Energy Density Matter (HEDM) Program Motivations

The performance limits of current propellants have been reached

- The constituents of current propellants have been known for decades
- The US is falling behind other countries in developing new energetic materials (e.g., Russians discovered ADN in the 1970s)

A revolutionary propulsion source would substantially improve our ability to access and control space

- Fusion, antimatter, and beamed energy are tantalizing yet distant prospects
- Novel chemical propellants offer the best potential for near-term improvements
- Chemical propulsion will remain the method of choice for many applications
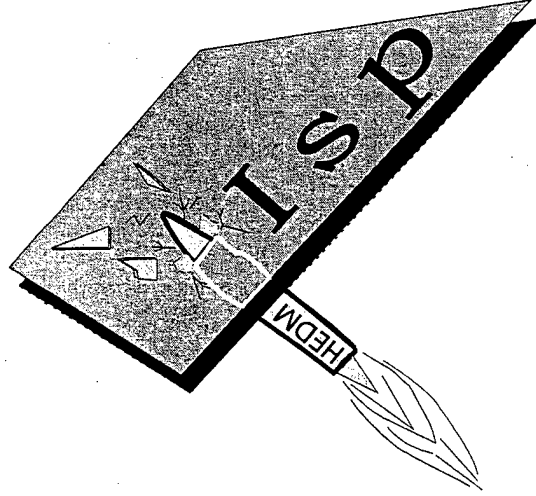
Developing high energy density materials as propellants is a vital and revolutionary technology

- "The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants." -- New World Vistas Panel on Space Technology
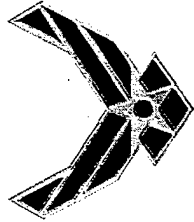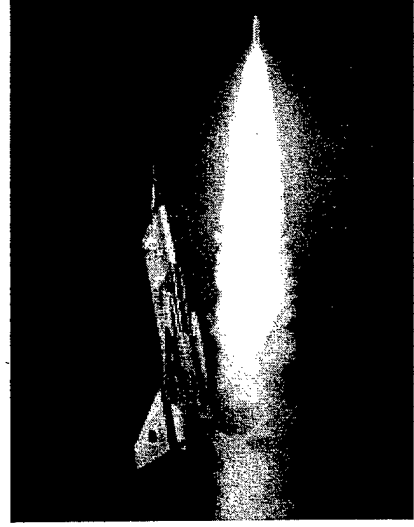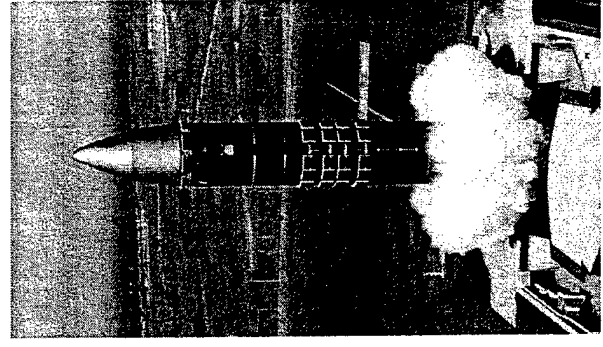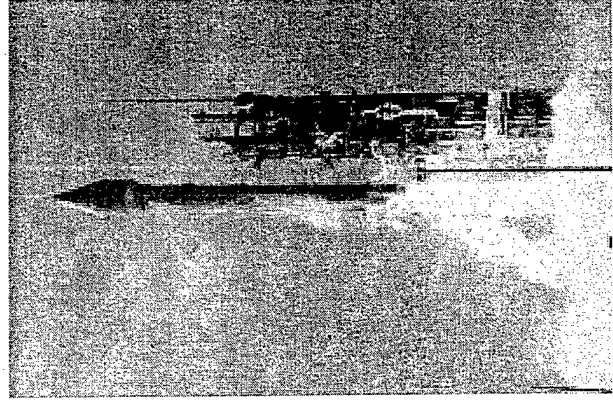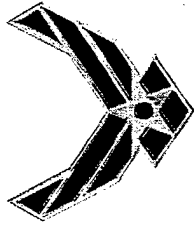
HEDM Program Objective

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites

I s p

HEDM

Breaking the performance barrier

Current State of the Art

	Isp (sec)	Density (g/cm³)
Monopropellants		
Hydrazine (N_2H_4)	233	1.01
Hydrogen Peroxide (H_2O_2)	175	1.41
Solids		
Ammonium Perchlorate (AP)	260	1.69
~20%Al/~10% polymer binder		
Liquids		
N_2O_4/Hydrazine	280	1.45/1.01
RP-1/Liquid Oxygen (LOX)	300	0.81/1.15
Cryogenic		
Liquid Hydrogen (LH2)/LOX	390	0.07/1.15

I_{sp} at sea level 1000 psi chamber pressure

Isp = (pounds of thrust/pounds of propellant/second)
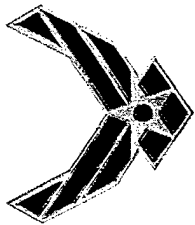
HEDM Propellant Payoffs

"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants."
-- New World Vistas Panel on Space Technology (1995)

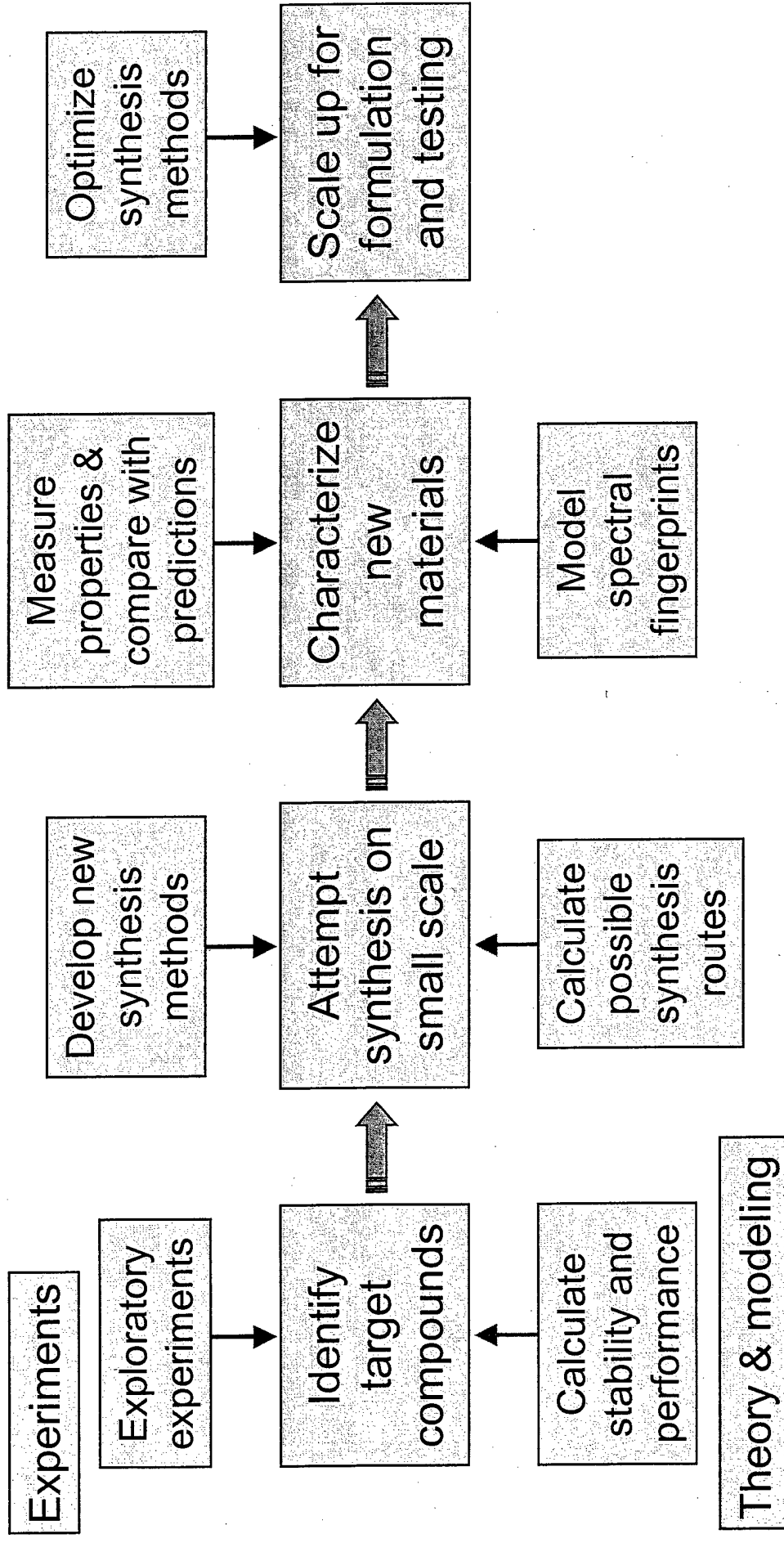| Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (**+25%**)
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (**+70%**)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 (**+49%**)

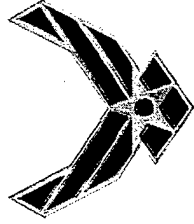*Our research is aimed at increasing propellant Isp by 5 to 50%*
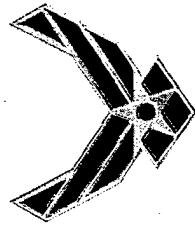
HEDM Program General Approach

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics

Experiments

Theory & modeling

Exploratory experiments →	Identify target compounds ←	Calculate stability and performance
Develop new synthesis methods →	Attempt synthesis on small scale ←	Calculate possible synthesis routes
Measure properties & compare with predictions →	Characterize new materials ←	Model spectral fingerprints
Optimize synthesis methods →	Scale up for formulation and testing	

The Calculation of Molecular Properties

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i\sum_{j>i} \frac{1}{r_{ij}} \right]\Psi_{el} = E_{el}\Psi_{el}$$

Determining what to synthesize:

Potential-energy surfaces – energy profiles associated with all degrees of freedom in a chemical system – give insight into stabilities and reaction & decomposition pathways

Thermodynamic properties relate directly to propellant performance and are obtained from relative energies of reactants, intermediates, and products

Determining whether we've made what we wanted to make:

Structures and spectra (IR, Raman, NMR) are obtained by evaluating derivatives of the energy or other properties with respect to nuclear coordinates or applied fields
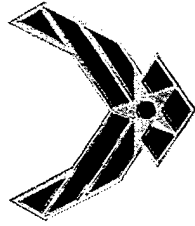
Quantum Chemical Methods

Wavefunction-based Methods

Energy obtained from QM wavefunctions: $E = \langle \Psi | H | \Psi \rangle$

Single configuration
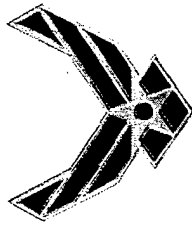
SCF RHF, ROHF, UHF

Dynamical MBPT, CI, CC
correlation

Multiconfigurational

TCSCF, GVB, MCSCF

CASPT2, MCQDPT,
MRCI, MRCC

Density-based Methods (DFT)

Energy obtained directly from density: $E = h + J + E_{xch}[\rho] + E_{corr}[\rho]$

The Computational Machinery

A variety of computer programs are used to perform the quantum chemical calculations, including:

- **GAMESS** (<u>G</u>aussian <u>A</u>tomic and <u>M</u>olecular <u>E</u>lectronic <u>S</u>tructure <u>S</u>ystem), from Iowa State University (Mark Gordon).

- **ACES** II (<u>A</u>dvanced <u>C</u>oncepts in <u>E</u>lectronic <u>S</u>tructure), from University of Florida (Rod Bartlett), with several custom modifications made by AFRL/PRS researchers

- **GAUSSIAN 98**, from Gaussian, Inc. (John Pople)

- **MOLPRO 98**, from University of Birmingham (UK), with several custom modifications made by AFRL/PRS researchers

The HEDM program benefits greatly from the extensive AFOSR investment in the development of these tools
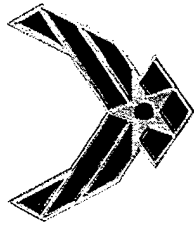
Polynitrogen Project

Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen allotropes

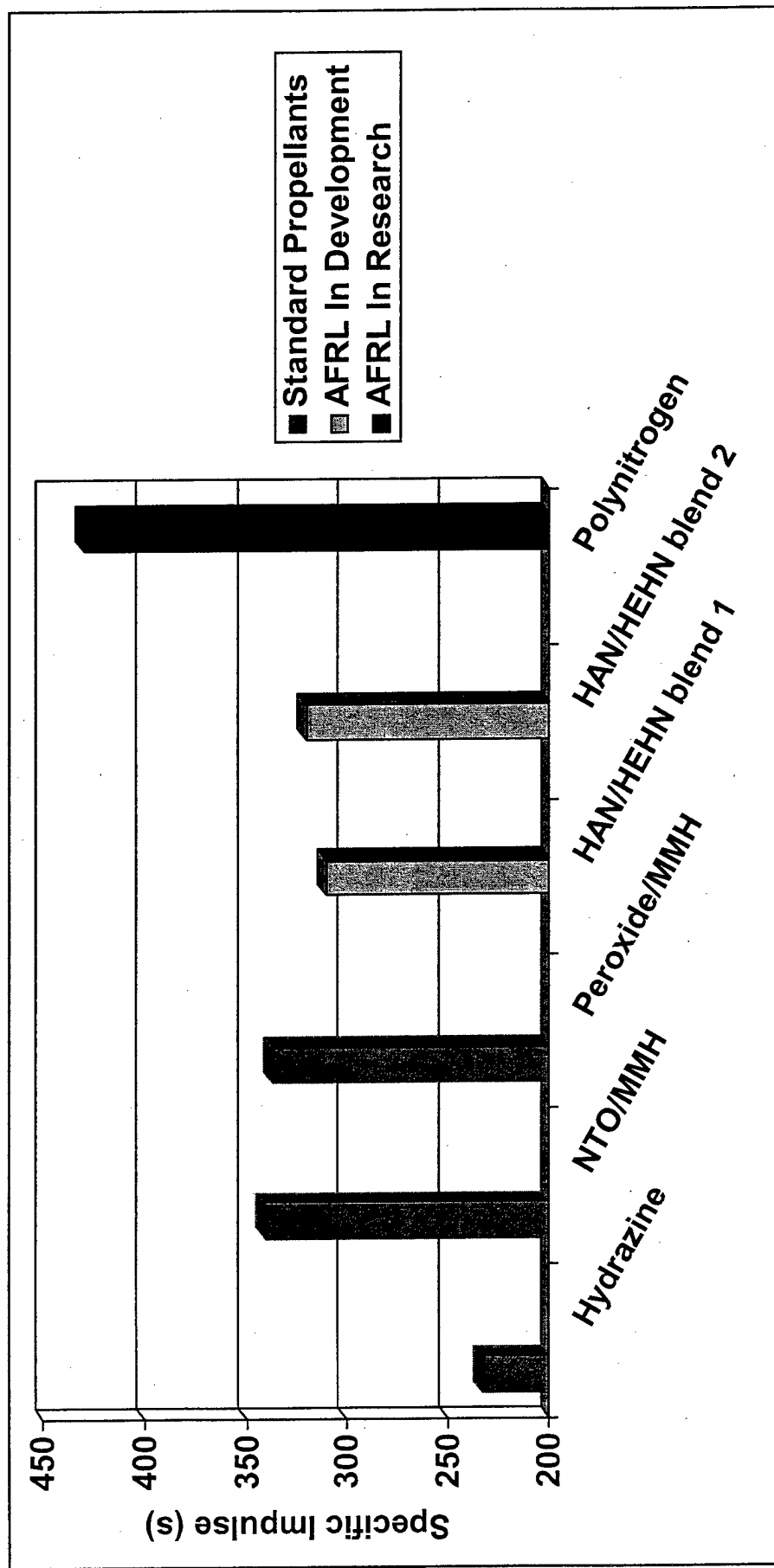*Modeling and simulation guides the experimental program:*

- Determines which molecules should exist and how energetic they are
- Gives information on how to synthesize promising molecules
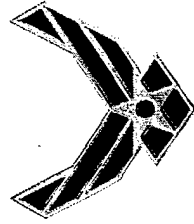- Provides critical data for identification and characterization of new molecules

ANGEWANDTE CHEMIE
INTERNATIONAL EDITION
1999/38
13/14
POLYNITROGEN HEDM
N_5^+
WILEY-VCH
InterScience
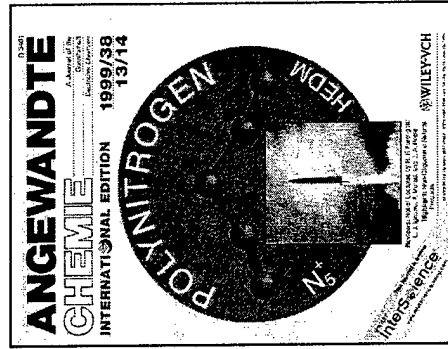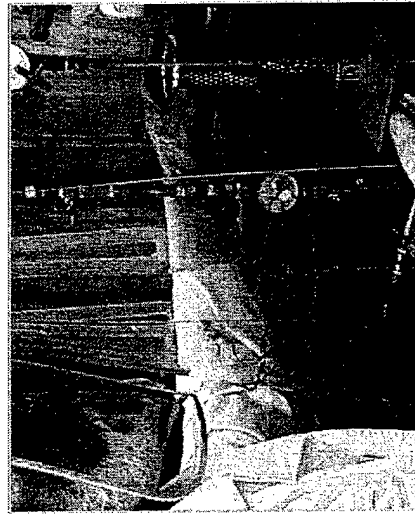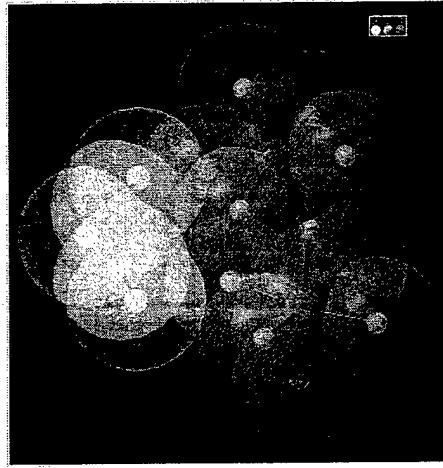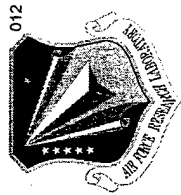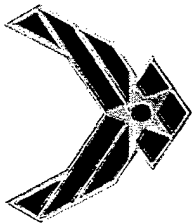
Performance of Polynitrogen Monopropellants

The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants

Specific Impulse (s)

- ■ Standard Propellants
- ▨ AFRL In Development
- ■ AFRL In Research

Hydrazine

NTO/MMH

Peroxide/MMH

HAN/HEHN blend 1

HAN/HEHN blend 2

Polynitrogen

450 400 350 300 250 200

The Search for New Polynitrogens

- All polynitrogens are unstable with respect to N_2 molecules

- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound

- Their metastability is enhanced if suitable resonance structures exist:

$$[|\overline{N}-N\equiv N|]^- \longleftrightarrow [\overline{N}=N=\overline{N}]^- \longleftrightarrow [|N\equiv N-\overline{N}|]^-$$
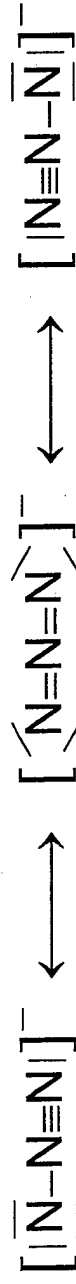
- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability

- How can this stabilization effect be used to our advantage in preparing new compounds?
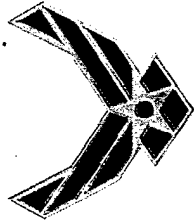
Pentazolate (N_5^-)?

- Substituted pentazoles R-N_5 have been known for decades (R=aryl)

- Cyclic N_5^- is aromatic

- Conversion of the diazonium salt, RN_2^+, to the substituted pentazole ring R-N_5 by the reaction with azide ion, N_3^-, has been demonstrated many years ago by Ugi and Huisgen.

- N_5^- has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).

- Can a chemical route to N_5^- be found? (e.g., can a suitable R group be found for the reaction R-N_2^+ + N_3^- -> R-N_5 -> R^+ + N_5^-? (For R=aryl, R-N_5 -> R-N_3 + N_2)
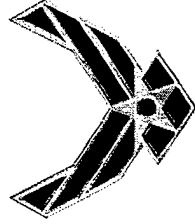
New Polynitrogen Anions
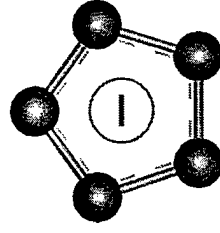
Pentazole anion (N_5^-)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic

- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas
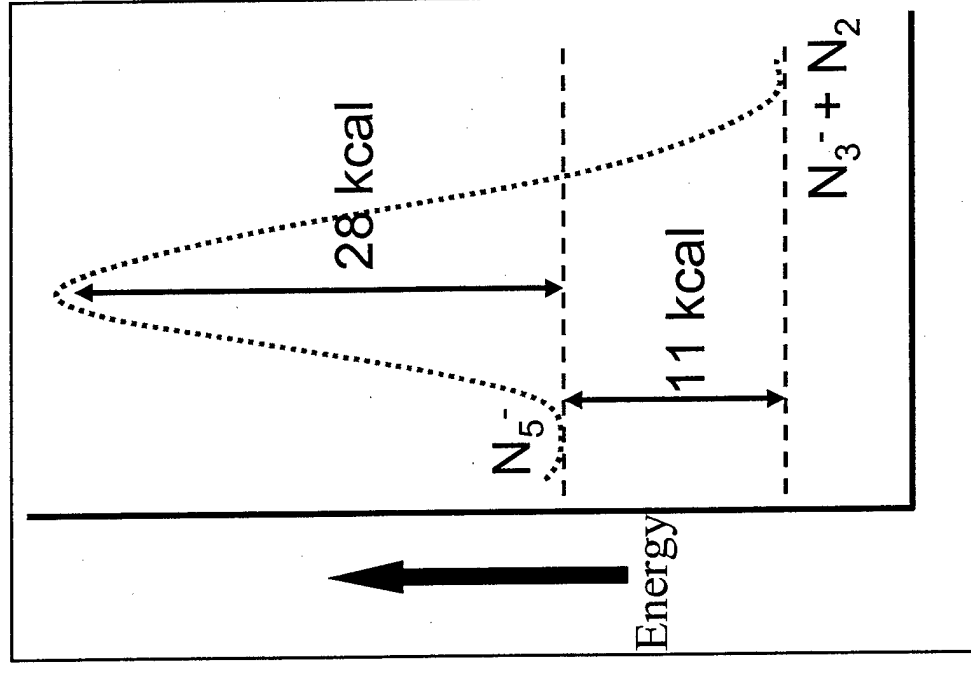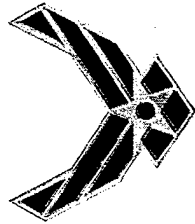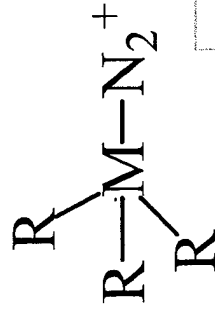
Synthetic Challenge – How do we make These New Anions??

Synthesis of Substituted Pentazoles

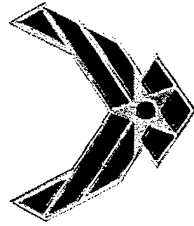### Sources for the Pentazole Anion (N_5^-)

Trityl/Silyl Diazonium Salts

Aryl Diazonium Salts

$R-M-N_2^+$ (with R, R groups), $M = C$ or Si

$+N_3^-$

Unknown

$Ar-N_2^+$ with $R\rightarrow$

$+N_3^-$
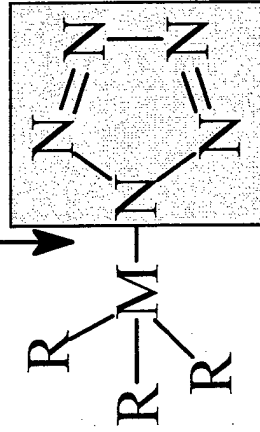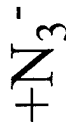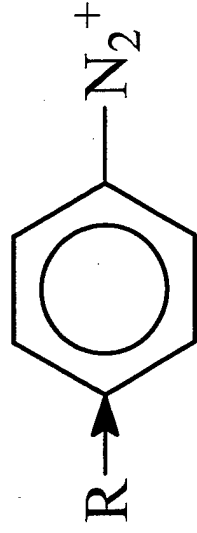
R = electron releasing group
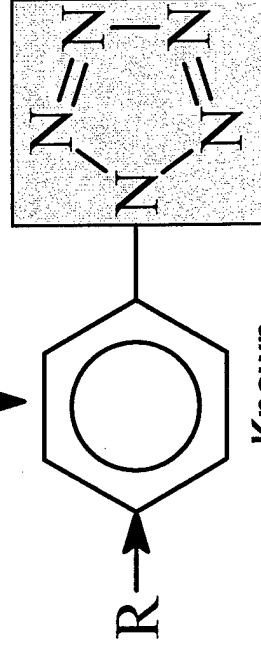
Known

Use of Aryl Diazonium Salts?

$$R\text{–}\bigcirc\text{–}N_2^+ X^- \;+\; N_3^- \longrightarrow R\text{–}\bigcirc\text{–}N_5 \;+\; M^+X^- \longrightarrow M^+N_5^- + R\text{–}\bigcirc\text{–}X$$
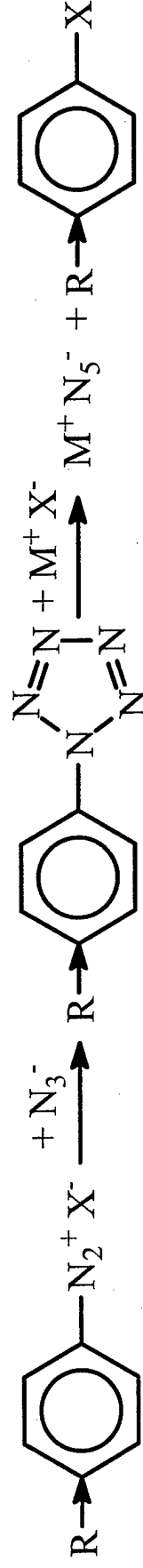
- R must be an electron releasing group, i.e., $-NMe_2$, $-OH$, $-OCH_3$, $-OC_6H_5$, $-O^-$, etc.

- Some of these substituted arylpentazoles have been known for about *four* decades but **no success** had been achieved to cleave the N_5 ring from the aryl group

Aryl Pentazoles can rapidly lose N_2 at room temperature

$$R\text{–}\bigcirc\text{–}N_5 \xrightarrow{-N_2} R\text{–}\bigcirc\text{–}N=N=N$$
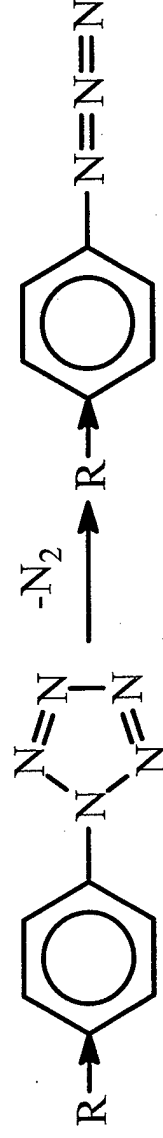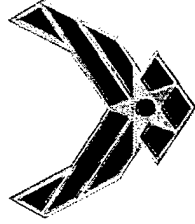
Theoretical Challenge - Can we design and predict viable precursors to N_5^-?

Find a substituent R so that

1. $R-N_2^+$ is stable wrt $R^+ + N_2$.

2. The R-N bond in $R-N_5$ is weak (less than ~28 kcal/mol), suitable for the reaction $R-N_5 + M^+X^- \rightarrow M^+N_5^- + R-X$
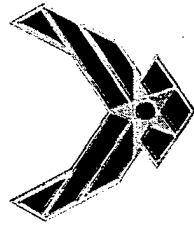
Approach

Use quantum chemical calculations to predict the stability of diazonium salts and the strength of the M-N bond.
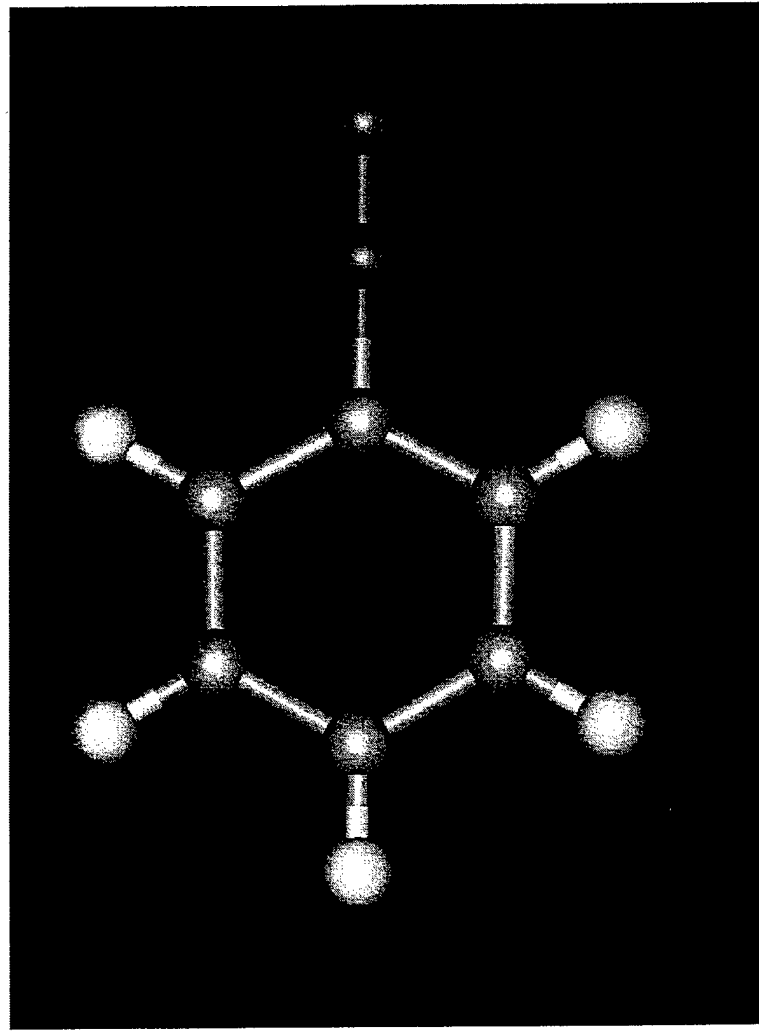
MBPT(2)/6-31G(d) level of theory

$$L_3M-N_2^+$$

M = C, Si

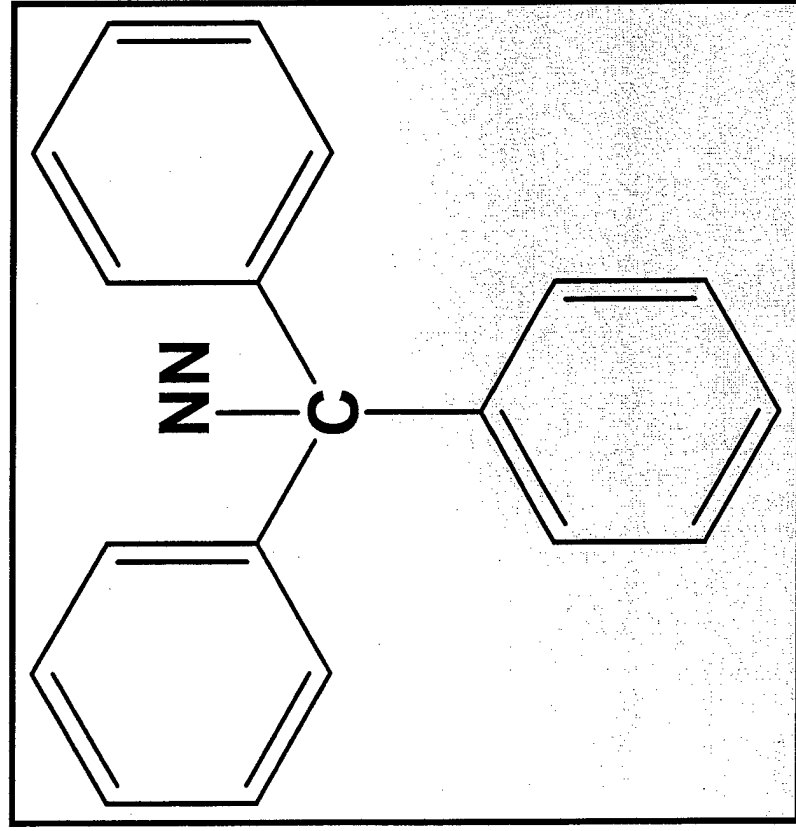L = F, Cl, CH_3, CF_3, NO_2, phenyl, etc.

Phenyldiazonium -- too stable!

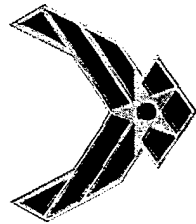R(C-N) = 1.39 Å

D_e = 37.9 kcal/mol

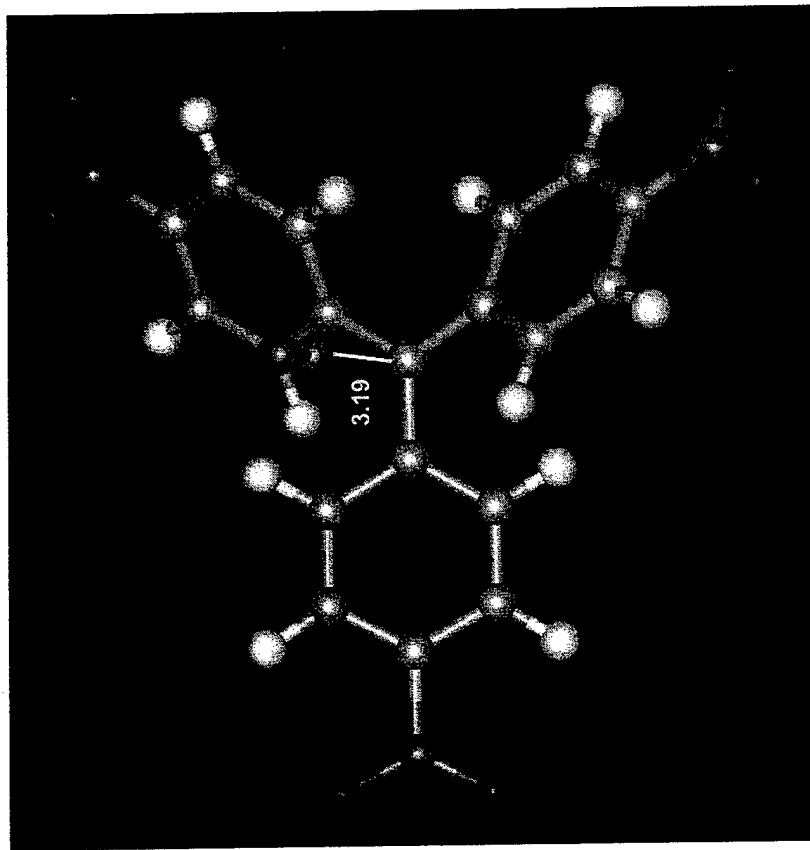Try replacing Ph+ with a more stable cation (Ph_3C^+)...
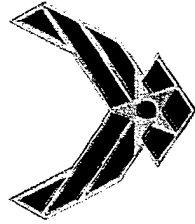
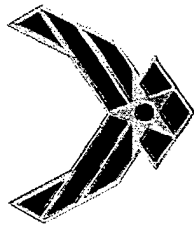# *Trityldiazonium -- unstable!*
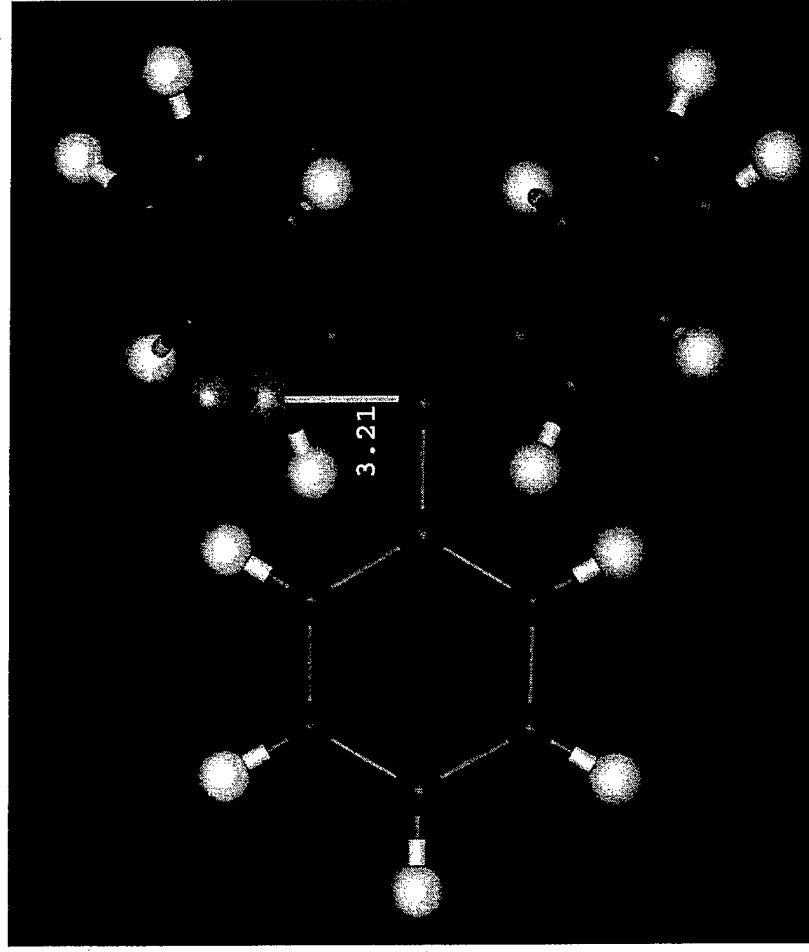
Trityl cation Ph_3C+ is too stable -- can it be destabilized by placing e-withdrawing groups on the phenyl rings (e.g. NO_2)?

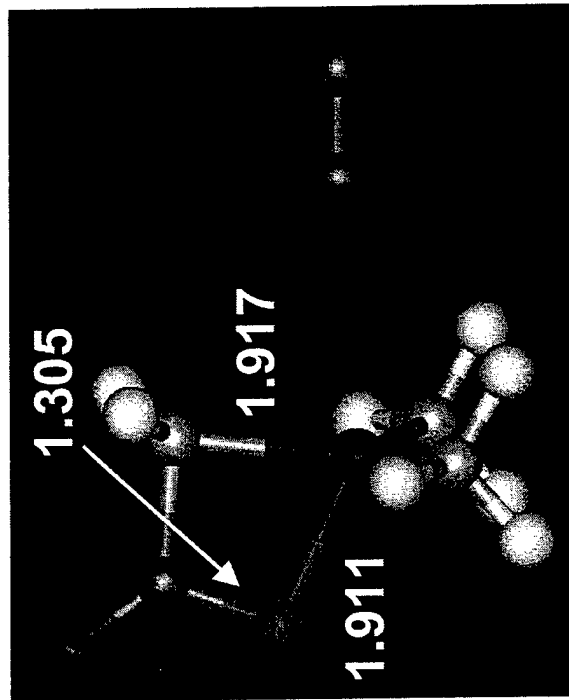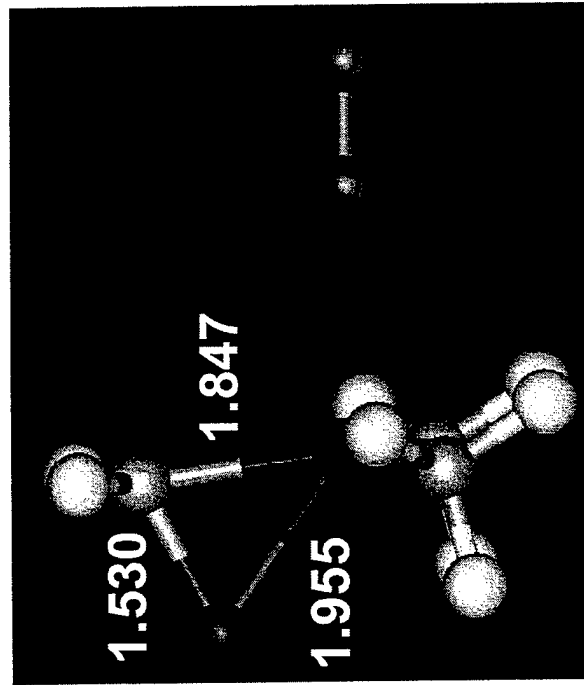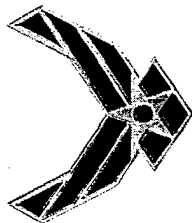# tris(para-nitrophenyl) methyldiazonium

R3	R3C-N distance(Å)	D_e(C-N) (kcal/mol)
3Ph	> 3.0	-3.0
3(pNO2-Ph)	> 3.0	-3.4

What about some silicon analogues?

R₃	R₃Si-N distance(Å)	Dₑ(Si-N) (kcal/mol)
3Ph	> 2.5	-6.0
3Me	2.151	-13.8
2Me,FCH₂	2.410	-7.4
2Me,NO₂CH₂	> 2.5	-5.2

Silicon analogues, continued

| R_3	R_3Si-N distance(Å)	D_e(Si-N) (kcal/mol)
3F	1.973	-33.4
3Cl	2.125	-14.5
3CF_3	1.994	n/a
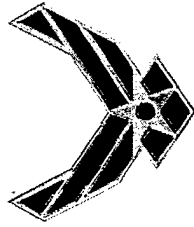
Conclusions

- Trityldiazonium ($Ph_3C-N_2^+$) and its tris(para-NO_2) analogue are predicted to be unstable wrt dissociation of N_2

- $Ph_3Si-N_2^+$ is also predicted to be unstable wrt dissociation of N_2

- $Me_3Si-N_2^+$ and $Cl_3Si-N_2^+$ are marginally stable ($D_e \sim 14$ kcal/mol; $R(Si-N) \sim 2.1$ Å)

- Of the silicon moeities considered, $F_3Si-N_2^+$ is the most stable ($D_e = 33.4$ kcal/mol; $R(Si-N) = 1.97$ Å)

- Secondary (i.e., not directly bonded to Si) electronegative groups such as F and NO_2 interact strongly with Si, leading to displacement of N_2
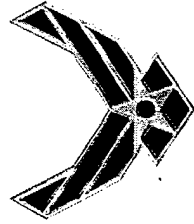
Future/ongoing work

- Calculations of the structures and stabilities of $Me_xF_yCl_zSi-N_2^+$

- Calculations of the structures and stabilities of R_3Si-N_5

- Other high-nitrogen/polynitrogen species (e.g. $Fe(N_5)_2$)
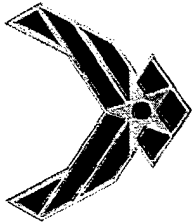
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